

REAL TIME DETECTION OF SODIUM IN SIZE-SEGREGATED MARINE AEROSOLS

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LONG-TERM GOALS

The long-term goal of this project is to develop a new capability for characterization of marine aerosols, specifically, the capability to make near real-time sodium measurements on individual size-segregated marine aerosols. It involves the development of a field-ready instrument which could carry out the proposed measurements from land based, shipboard or airborne platforms. Such an instrument would allow us to measure the size distribution of seasalt aerosols in air in a variety of sea states and to verify laboratory-derived relationships for the formation of aerosols via sea spray bubble bursting mechanisms. Ultimately, the development and deployment of such an instrument would improve our understanding of the size distribution of seasalt aerosols in marine air and provide data for relating the abundance of these aerosols to remotely observable parameters related to the physical state of the atmosphere and surface ocean. It would allow us to calculate the influence of seasalt-derived particles on the optical properties of the marine aerosol and characterize and predict the variability of this signal.

OBJECTIVES

Our objective is to determine the feasibility of coupling aerosol detection and sizing instrumentation with a highly sensitive spectroscopic sodium detector utilizing laser induced fluorescence. This would allow the simultaneous quantitative determination of aerosol size and sodium content. For our initial feasibility study, we are attempting to build a system and determine its detection limits using small well-characterized sodium chloride particles.

APPROACH

The principle difficulty in the real-time chemical analysis of submicron aerosols is the steep decline in mass with decreasing diameter of individual particles. Several methods and combinations of methods will probably be necessary to select and analyze particles since no one technique is adequate to deal with the range of sizes and concentrations of seasalt found in the marine atmosphere. In order to provide a "baseline" for intercomparison of techniques, we have developed a reproducible source of monodisperse sodium chloride aerosols with diameters in the

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0.5 to 8 μm range. For most experiments, we have used 2 μm aerosols; this represents a good size compromise because it can be detected optically by scattered light and accurately sized using both differential mobility and aerodynamic particle sizers. Sodium chloride is detected by conversion to atomic sodium in a plasma or flame, and monitoring its emission at 589 nm or its laser induced fluorescence signal using an excimer-pumped dye laser as the excitation source.

WORK COMPLETED

A monodisperse small particle source based on a vibrating orifice aerosol generator (voag) has been built. The voag generates a stream of monodisperse droplets by forcing dilute sodium chloride solutions at pressures of 20 - 40 psi through a 20 μm diameter droplet forming platinum orifice which is vibrated by a piezo electric crystal to control the rate of droplet formation. Depending on the applied frequency, the droplets initially formed are on the order of 100 - 120 μm in diameter. The droplets flow through a drying tube with filtered dry compressed air, producing dried 0.5 - 8 μm sodium chloride particles depending on the initial droplet size and NaCl concentration. For most experiments, we use 2 μm particles and have optimized residence time and humidity to minimize fracture of the dried particles and generate an essentially monodisperse 2 μm particle stream.

We have tried two approaches to convert sodium chloride to atomic sodium. Firstly, we have constructed a high pressure microwave discharge which operates between 50 and 700 Torr depending on gas mixture. The aerosol/air mixture at atmospheric pressure passes through an orifice which drops the pressure to 50 Torr before passage through the microwave cavity. In the cavity, a microwave discharge generates a plasma with temperatures high enough to convert NaCl to Na atoms. In the second approach, the aerosol passes into a flame stabilized on a flat flame burner constructed in this laboratory; again, temperatures in the air/methane or air/acetylene flame are sufficient to convert NaCl to its constituent Na atoms.

Aerosol particles in this size range are reliably detected by monitoring the scattered light generated as they pass through the $\sim 20\mu\text{m}$ focus of a 633 nm diode laser beam. We have built an amplifier and associated electronics system to reliably trigger the laser and/or detection system using a single aerosol's scatter signal. The burner was built with a scattering chamber 4 cm below the flame front to allow optical detection of the aerosol before the particle hits the flame front.

RESULTS

In experiments using the microwave discharge, the plasma emission spectrum was monitored using an optical multichannel analyzer. In an air discharge we see a strong molecular emission band from 580-595 nm which overlaps the Na D-line emission. After background subtraction, a D-line signal is observable from the very large numbers of sodium chloride aerosols generated by a pneumatic nebulizer but no signal was observed from the 2 μm particle stream under the same conditions (the voag generates about 1000 times fewer particles/min than the nebulizer, and hence would give much lower concentrations in the discharge). By contrast, clear D-line emission signals are observable from single 2 μm particles from the voag in the burner configuration. Since the flame appears to be more efficient at converting NaCl to Na atoms than

the microwave discharge, the rest of our experiments utilize this conversion technique.

In an initial series of experiments, we compared sodium detection limits by aspirating NaCl solutions into an air/acetylene flame and found that single photon laser induced fluorescence is at least two orders of magnitude more sensitive than D-line emission at 589 nm from the thermally excited state. We tried a number of different laser excitation/monitoring wavelength schemes, but the most favorable to date is simple excitation of the D-line at 589.0 nm with monitoring of the excited state fluorescence at 589 nm using a bandpass filter. Experiments are underway to establish detection sensitivity for single aerosol particles in the burner configuration using this single photon laser induced fluorescence detection scheme.

IMPACT

This is the first year of this project and our initial results suggest that the approach is a promising route to the characterization of marine aerosols. Clearly however a field operable instrument is required to assess the impact of this study on our understanding of marine boundary layer particle formation.

TRANSITIONS

As this is a very preliminary phase of this project, it is too early to see transitions from this work into the Navy fleet or industry, but we see a strong future for real-time analytical instrumentation for ship-board environmental measurements.

RELATED PROJECTS

In related ONR, NSF and NASA sponsored work we are investigating several aspects of the basic chemistry of the marine boundary layer which are important for visibility and particle formation issues. These include the sources and chemistry of the sulfur species which lead to non sea salt sulfate aerosol and the basic atmospheric chemistry which drives gas to particle conversion.